

AD-A109 477

TEXAS UNIV AT AUSTIN DEPT OF CHEMISTRY
THE DESIGN OF SEMICONDUCTOR PHOTOCHEMICAL SYSTEMS FOR SO-ETC(U)
DEC 81 A J BARD

N00014-78-C-0592

ML

UNCLASSIFIED

TR-20

F/8 20/12

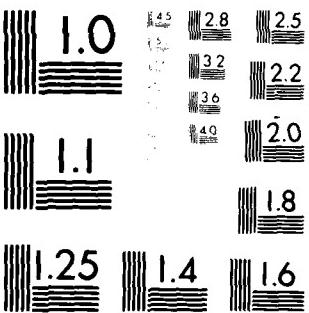
END

DATE

FILED

12

NTIC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS 1964 A

(12)

OFFICE OF NAVAL RESEARCH

Contract N00014-78-C-0592

Task No. NR 051-693

TECHNICAL REPORT No. 20

LEVEL II

ADA109477

THE DESIGN OF SEMICONDUCTOR PHOTOLELECTROCHEMICAL
SYSTEMS FOR SOLAR ENERGY CONVERSION

by

Allen J. Bard

Prepared for Publication

in the

Journal of Physical Chemistry

DTIC

2010 3 382

M

The University of Texas at Austin
Department of Chemistry
Austin, Texas 78712

December 21, 1981

Reproduction in whole or in part is permitted for
any purpose of the United States Government.

This document has been approved for public release
and sale; its distribution is unlimited.

DTIC FILE COPY

82 000001

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 20	2. GOVT ACCESSION NO. 4D-A109 477	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) The Design of Semiconductor Photoelectrochemical Systems for Solar Energy Conversion		5. TYPE OF REPORT & PERIOD COVERED 9/1/81 - 8/31/82
7. AUTHOR(s) Allen J. Bard		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry University of Texas at Austin Austin, TX 78712		8. CONTRACT OR GRANT NUMBER(s) N00014-78-C-0592
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research 800 N. Quincy Arlington, VA 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		12. REPORT DATE December 21, 1981
		13. NUMBER OF PAGES 35
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) This document has been approved for public release and sale; its distribution is unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES Prepared for publication in the Journal of Physical Chemistry		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The principles and applications of semiconductor electrodes in photoelectrochemical (PEC) cells for carrying out useful chemical reactions are described. The factors in the design of efficient and stable systems and semiconductor particulate systems constructed on the basis of PEC cell principles are discussed.		

DD FORM 1473 JAN 73

EDITION OF 1 NOV 65 IS OBSOLETE
I/N 0102-014-6601

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

THE DESIGN OF SEMICONDUCTOR PHOTOLELECTROCHEMICAL
SYSTEMS FOR SOLAR ENERGY CONVERSION

Allen J. Bard

Department of Chemistry

The University of Texas

Austin, Texas 78712

(ABSTRACT)

The principles and applications of semiconductor electrodes in photoelectrochemical (PEC) cells for carrying out useful chemical reactions are described. The factors in the design of efficient and stable systems and semiconductor particulate systems constructed on the basis of PEC cell principles are discussed.

Accession For	
NTIS GRAM	X
DTIC TAB	
Unnumbered	
Justified	
By	
Distributed	
Available	3
File No.	
Dist S	
A	

Submitted to J. Phys. Chem., September 22, 1981

The efficient production of fuels from inexpensive precursors by utilization of solar energy with cheap and stable chemical systems has become the goal of numerous research efforts. Examples of desirable reactions are the reduction of water (or protons) to H₂ and the reduction of CO₂ to methanol driven by light. Because the effect of light in any system is the creation of electron-hole (e⁻h⁺) pairs, the fuel-producing reaction must be accompanied by an oxidation reaction. This oxidation reaction should consume an inexpensive or waste material (e.g., produce oxygen from water), or alternatively produce a substance of some value (e.g., Cl₂ from Cl⁻ oxidation). The model often used for such systems is biological photosynthesis, in which light is utilized to produce reduced (carbonaceous) materials and O₂. However, the field efficiencies of biological systems, in terms of conversions of solar energy to fuel value, is rarely better than 1% and the individual systems do not show long lives (but they are, of course, self-replicating). Man-made photosynthetic fuel-producing systems will have to show at least an order-of-magnitude better efficiency as well as lifetimes of many years.

A number of photochemical and thermochemical schemes have been proposed to effect such light-driven reactions. Among the most successful have been those involving the absorption of light and the occurrence of electron transfer reactions at the semiconductor/liquid interface. The basic principles and examples of such liquid junction semiconductor devices have been the subject of a number of reviews.¹⁻⁵ I will emphasize in this paper the concepts involved in designing semiconductor photoelectrochemical (PEC) systems, the recent research of our group, and some of the problems that still remain.

The general scheme for the construction of a photoelectrochemical

system involving a single light absorber is shown in Figure 1. The energetics of the system, in terms of electron energy levels and redox potentials are given in Figure 2. In general the overall reaction involves the following stages:

- (1) Photon capture and $e^- h^+$ pair formation (1,2).
- (2) Trapping of e^- and h^+ in rapid chemical reactions (3,5).
- (3) Catalytic formation of final products (4,6) and separation.

Light is captured in the light-absorbing system (1,2) which represents a support material and the sensitizer layer. This could be a metal substrate with a thin layer of semiconductor (e.g., TiO_2 on Ti), a transition metal complex, or an organic dye sensitizer on a semiconductor substrate (e.g., $Ru(bpy)_2^{2+}$ or ZnPc on TiO_2 ; where bpy is 2,2'-bipyridine and Pc is phthalocyanine). The light-absorbing system serves to convert the incident photons into electron-hole pairs and frequently provides a gradient in electrical or chemical potential to cause separation of e^- and h^+ . Recombination of e^- and h^+ is also prevented if they are transferred rapidly to suitable acceptor, A(3), or donor, D(5), molecules. The couple represented by A/A^- (e.g., MV^{2+}/MV^+ or S_x^{2-}/S^{2-} ; where MV^{2+} is methyl viologen) should have as negative a redox potential as possible, consistent with rapid reaction with the photogenerated electron. It is unlikely that the fuel-producing reaction can occur directly at this stage, since these reactions frequently involve multielectron transfers and high energy intermediates. Similarly the D/D^+ couple (e.g., Br^-/Br_2 or Fe^{2+}/Fe^{3+}) should be as positive as possible consistent with rapid reaction of the photogenerated h^+ . The A/A^- and D/D^+ couples are sometimes called "relays", since they serve to transmit the photoproduced charges to the final desired electron transfer reactions. As shown in Figure 2 formation of A^- and D^+ results in some degradation of the energy of the $e^- h^+$ pair. The spontaneous

back electron transfer reaction between A^- and D^+ must be prevented by keeping them spacially separated or by having them react rapidly in a subsequent step. Similarly any reaction of A^- with h^+ or D^+ with e^- represents a loss in efficiency. The reaction of A^- to form fuel (e.g., $H^+ \rightarrow H_2$) usually will require a catalyst, CAT_R (4), which serves to couple the $A^- \rightarrow A$ and H^+ reduction reactions and provide a surface for adsorbed intermediates. Similarly an oxidation catalyst, CAT_O (6), will usually be required to couple the $D^+ \rightarrow D$ and the terminal oxidation (e.g., $H_2O \rightarrow O_2$) reaction. These catalyzed reactions again represent some degradation of the initial photon energy and again back reactions (e.g., A^- or e^- with O_2) must be prevented. The total energy of the products, ΔG_p° , is less than the energy of the captured photon, given by the band gap of the light-absorber, E_g , by the needed driving forces (or overpotentials) of the various electron transfer steps. Thus if ΔG_p° is ~ 1.3 eV (representative of many fuel-forming reactions) and each electron transfer step involves a ~ 0.2 eV overpotential, then E_g must be greater than 2.1 eV.

Principles of Semiconductor Electrodes

The principles of semiconductor electrodes as applied to photoelectrochemical cells have been discussed in a number of reviews¹⁻⁷ and will only be outlined here. Basically a space charge layer forms at the semiconductor/liquid interface as the two phases come into electronic equilibrium (i.e., as the Fermi levels or electrochemical potentials become equal) (Figure 3). The electric field in this space charge region serves to separate the e^-h^+ pairs produced by light absorption. The direction of the field is usually such that holes move to the surfaces at n-type semiconductors and lead to oxidations while electrons move to the surface at p-type semiconductors and cause reductions. The primary energetics of the

system can be obtained from a knowledge of the flat band potential (which for highly-doped semiconductors approximately corresponds to the location of the conduction band edge, E_c , in n-type semiconductors and the valence band edge, E_v , in p-type) and the band gap energy, E_g . Typical values for n-TiO₂ and p-GaAs are shown in Figure 3. However, for a given semiconductor, the location of these energy levels depends upon the nature of the solvent, the presence of ions which adsorb on or react with the semiconductor surface, and the presence of surface states or surface charge which leads to non-ideal behavior such as Fermi level pinning or inversion. However, at least as a first approximation, it is useful to consider that under irradiation holes and electrons are delivered at potentials corresponding to E_v and E_c , respectively. A PEC cell with a single absorbing semiconductor system and a metal or carbon counter electrode thus can represent the general system of Figure 1 with $e^- h^+$ separation driven by the electric field in the space charge region and spacial separation of products preventing back reaction.

Design of Semiconductor PEC Cells

The design of a practical photoelectrosynthetic cell (a PEC cell which converts radiant energy to chemical free energy) is based on both semiconductor and solution properties.

1. Band gap energy. The value of E_g should be as small as possible consistent with driving the desired overall cell reaction. The maximum efficiency for terrestrial solar energy utilization occurs for a E_g of 1.1 to 1.3 eV, although values up to ~ 2.0 eV can be used with reasonable efficiencies.⁸

2. Band edge locations. The values of E_c and E_v , as represented by the corresponding redox levels, must be compatible with the desired half

reactions (A/A^- and D^+/D). The location of these levels depends not only on the inherent work function of the semiconductor, but also upon the nature of the solvent and specific adsorption of ionic charge at the interface. The band edge locations are frequently estimated from the flat band potentials determined from plots of the interface capacitance with potential (Mott-Schottky plots) or, somewhat less reliably, from the potential for the onset of the photocurrent.

3. Stability. Both the thermodynamic and kinetic factors involved in stability of the semiconductor have been discussed.^{9,10} The problem appears more acute with n-type materials where the photogenerated holes, which move to the interface, are capable of oxidizing the semiconductor itself. For example, with ZnO in an aqueous solution at pH = 0 the half-reaction $ZnO + 2h^+ \rightarrow Zn^{2+} + \frac{1}{2}O_2$ ($E_D^\circ = +0.9$ V vs. NHE) can occur readily with holes produced at the potential of the valence band edge (~ 3.0 V vs. NHE). Thus irradiation of a ZnO electrode in an aqueous solution will cause at least partial decomposition of the semiconductor electrode. A number of approaches have been taken to stabilize the semiconductor. By proper choice of the D^+/D couple the photogenerated holes can be removed rapidly before decomposition can occur. If the standard potential of the D^+/D couple is more positive than E_D° , a direct attack by D^+ on the semiconductor is thermodynamically possible, however. It also appears that a thick layer of metal or conductive polymer on the electrode surface can serve to remove the photogenerated charge rapidly and stabilize the material.¹¹ If the solvent is changed to a nonaqueous one or the water activity is greatly decreased, E_D° can be made more positive and the stability enhanced. Experiments are also under way on the modification of semiconductor surfaces, e.g., by derivatization or polymer coating techniques, in attempts at improving stability.¹² For example, unprotected n-silicon in aqueous solutions forms

an insulating oxide film under irradiation in aqueous solutions. However, when it is covered with a thin metal layer (Au or Pt) and a thicker polypyrrole film, it behaves as a stable photoanode in I^-/I_3^- and Fe^{2+}/Fe^{3+} solutions.¹³ These films probably serve to protect the semiconductor by removing the photogenerated h^+ and also by making the surface more hydrophobic. Some water penetration to the surface must still occur, however, since the addition of strong electrolyte (e.g., 11 M Li Cl) to the solution to decrease water activity improves the stability even more.^{13a} The technique of using high concentrations of electrolyte to decrease water activity while still providing a medium with high conductivity was used first by Wrighton, *et al.*,¹⁴ to stabilize n-MoSe₂ during the photogeneration of chlorine in chloride media.

Although p-type materials can be reduced by the photogenerated electrons brought to the electrode surface (e.g., p-Cu₂O in aqueous electrolytes), in general they tend to be more stable in aqueous media than n-type and are, in fact, self-cathodically protected from oxidation.¹⁵ The reduction of the p-type materials can also be suppressed by the use of nonaqueous media. For example, p-type Cu₂O can be employed in the reduction of nitrobenzene to its radical anion in acetonitrile.¹⁶

4. Doping level. The thickness of the space charge layer and the resistance of the bulk semiconductor are controlled by the doping level. This can be adjusted so that the space charge layer extends sufficiently deep that essentially all of the incident light is absorbed within it. Higher doping of the bulk semiconductor is desirable, and n⁺n or p⁺p structures can be used to optimize efficiencies (where n⁺ and p⁺ refer to higher doping levels).

5. Crystallinity. From the standpoint of ease of production and low cost, polycrystalline semiconductor electrodes are needed. These have been

prepared by a number of techniques (e.g., chemical vapor deposition, vacuum evaporation, sputtering, electrodeposition) and in many cases show efficiencies approaching those of single crystal materials.

6. Surface treatment. The nature of the semiconductor surface can be an important factor in the efficiency, since surface states can act as $e^- h^+$ recombination centers. Thus different etching, chemical pretreatment and surface modification methods have been used to improve the cell performance. An example of this approach is the passivation of edges on n-WSe₂. Small single crystals of the layered compound WSe₂ show excellent photoelectrochemical efficiencies, when the surface is free from exposed edge planes. The presence of edges leads to significant dark oxidation currents and lower efficiencies. When these electrodes are employed to oxidize o-phenylenediamine, polymer formation occurs at the dark oxidation sites (presumably the edges), with greatly improved efficiencies in PEC cells.¹⁷ Similarly selective adsorption of appropriate species (e.g., tert-butylpyridine) onto the edge planes can improve the performance of the layered compounds.¹⁸

7. Redox couple. The redox couples chosen for A/A⁻ and D/D⁺ must satisfy a number of requirements. Both forms should be stable as well as highly soluble (>1 M) to prevent mass transport control of the current. The heterogeneous electron transfer rates should be rapid and the redox potentials appropriate to drive the desired final fuel-producing reaction at the catalyst and yet be located where photodriven charge transfer and stabilization of the semiconductor occur. They should be inexpensive and neither form should absorb light of energy above E_g.

Catalysis

Although the conduction band energy of several p-type electrodes (e.g.,

GaAs, Si) in aqueous electrolytes is at sufficiently negative values that direct reduction of protons to H₂ is thermodynamically possible, the hydrogen evolution reaction does not occur with good efficiency under illumination. This can be attributed to the slow reaction kinetics for hydrogen evolution at most electrode materials; in electrochemical terminology, most semiconductors show a high hydrogen overpotential. As depicted in Figure 4, formation of hydrogen atoms (H[•]) by the one-electron half-reaction requires a very negative potential. This energy can be overcome if H-atoms are adsorbed as they are, for example, on Pt. The energy of adsorption of H[•] on most p-type semiconductors is apparently small. As was demonstrated with both p-GaAs¹⁹ and p-Si,²⁰ the use of the rapid one-electron redox couple MV²⁺/MV⁺ and finely divided Pt promotes photogenerated hydrogen evolution. The Pt plays the role of a catalyst, and allows the pooling of electrons so that the electron transfer reactions 2 H[•] + 2 e⁻ → H₂ and MV⁺ → MV²⁺ + e⁻ can both occur at equal rates. An electrochemical model for this catalyzed electron transfer has recently been described.²¹

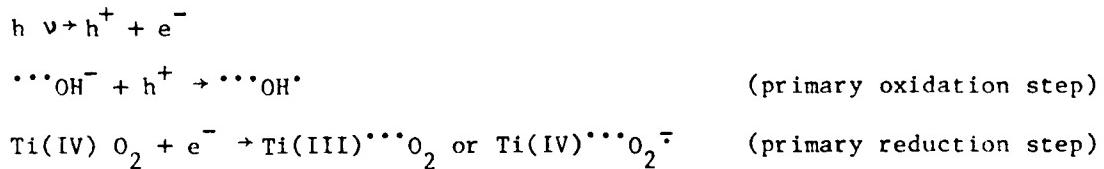
Direct oxygen evolution at semiconductors (e.g., n-TiO₂, n-Fe₂O₃, n-SrTiO₃) has been observed, but the valence band location in these is usually sufficiently positive that formation of the high energy intermediate, hydroxyl radical (OH[•]) appears possible. Indeed, spin trapping experiments demonstrate that at irradiated TiO₂ powders OH[•] is formed.²² The production of O₂⁺ utilizing an appropriate couple, D⁺/D, and/or a heterogeneous catalyst should be possible. Improved rates of oxygen evolution with RuO₂ as a catalyst have been reported.²³ As discussed earlier, stability of small band gap semiconductors with appropriately placed valence band edges (e.g., at ~+1.7 V vs. NHE at pH = 0 or ~+1.3 V at pH = 7) may be an important problem.

Other oxidation half-reactions, which are inherently more rapid and occur at less positive potentials, such as $2 \text{Br}^- \rightarrow \text{Br}_2 + 2 \text{e}^-$, may also be of interest. Another possibility is the use of "sacrificial" waste materials. For example, the photo-oxidation of acetate to produce ethane and CO_2 at $n\text{-TiO}_2$ occurs quite readily,²⁴ and acetate and other carboxylic acids are fermentation products obtainable from biomass. However, one should note that the overall reaction $2 \text{CH}_3\text{COOH} \rightarrow \text{C}_2\text{H}_6 + \text{CO}_2 + \text{H}_2$ occurs with $\Delta G^\circ < 0$, i.e., is thermodynamically downhill, so that the PEC cell reaction is really a photocatalytic (rather than an energy-storing photoelectrosynthetic) one.

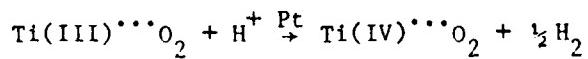
Particulate Systems

The principles of semiconductor PEC cells can be applied to the design of particulate or powder systems for carrying out photoreactions.^{1,2} For example, platinized TiO_2 powder in a rough sense can be visualized as a short-circuited photocell analogous to that of Figure 3. Light impinging on the TiO_2 again causes $e^- h^+$ pair formation and the Pt again appears to serve as an effective reduction site. While there have been few studies on the detailed mechanisms and physical-chemical nature of photoreactions at semiconductor powders in solution, a number of different photoreactions, including metal depositions, decarboxylations, polymerizations, and even small amounts of amino acid synthesis have been demonstrated.^{1,2} Reduction of CO_2 to methanol and other reduced species on irradiated TiO_2 , CdS , and CaP powders has also been reported,²⁵ although the overall efficiency for this reaction is quite low. Even the direct splitting of water to O_2 and H_2 has been accomplished with semiconductor/catalyst powders and colloids.²⁶ An electrochemical model can again be proposed for photoprocesses on semiconductor powders (Figure 5). However, the existence

of a real space charge region in the small, usually lightly-doped, particles is unlikely, and probably most charge separation occurs at the particle surface. Thus an alternative, more chemical way of looking at the photoprocess is as follows. Consider a TiO_2 particle. The $e^- h^+$ pair produced near the surface on irradiation forms, at least transiently, oxidized and reduced sites on the surface. Spin trapping experiments²² and the results of a number of photochemical studies (e.g., the formation of hydroxylated products during irradiation of benzene and benzoid acid) strongly indicate that the primary h^+ -trapping step is formation of hydroxyl radicals.^{27a} The nature of the reduced site is less certain. However, $Ti(III)$ species in solution have been identified during irradiation of TiO_2 powders in the presence of oxalate ion,^{27b} and this may represent the primary reduced species. The formation of a lattice O_2^- species also appears possible from gas phase studies of irradiated TiO_2 ²⁸ and spin trapping²² experiments. Thus the process can be written in chemical terms as:



Subsequent reactions of the oxidized and reduced forms lead to recombination or to the final products. Surface catalysts can promote these secondary reactions, e.g.,



The powder systems are of interest because they are inexpensive and relatively easy to fabricate. However, they do not offer the large spatial separation of the initially-produced oxidized and reduced forms of the PEC cells and the final products from particulate systems are formed as a

mixture rather than in separate streams. There are numerous studies of photoreactions at powders underway and new physical methods of characterizing the photoprocesses in solution (e.g., photoelectrophoretic,²⁹ electrochemical,²⁹ conductance,³⁰ and flash photolysis^{26b}) as well as powerful microscopic and spectroscopic methods of examining the powders in vacuum, are emerging.

The State-of-the-Art and the Future

The solar power efficiency of most photoelectrosynthetic systems with no input of external electrical energy is generally about 1 - 2% in terms of fuel value of products out vs. solar energy in. Photoassisted processes, where an electrical bias is applied to the PEC cell and both radiant and electrical energy are used to produce products, show higher efficiencies but are of less interest from a practical viewpoint. These photoelectrosynthetic efficiencies are 5 to 10 times smaller than those obtainable with liquid junction photovoltaic cells. Improvements in performance and practical cell construction require consideration of the following:

1. Energetics. As discussed in the introduction, consideration of the driving forces needed to carry out a fuel-producing reaction suggest that an $E_g \geq 2.1$ eV is required. This value is outside the range of maximum efficiency of solar energy utilization and can be contrasted to the smaller band gap materials used in photovoltaic cells (e.g., GaAs and InP; $E_g = \sim 1.3$ eV) where output voltage (usually < 0.6 V) is not a major factor. A suggested approach to the more effective utilization of solar energy is a dual light absorbing system,¹ depicted in Figure 6. In this case the needed energy can be obtained from two small band gap semiconductors ($E_g \sim 1.3$ eV) (Figure 7). While two photons are now required in this system to drive a

single electron through the redox chain, the smaller band gaps allow a much better match to the solar spectrum. The light absorbing systems could be two n-, two p-, or an n- and p-type semiconductor utilizing the O/R redox pair to couple to the two systems. An alternative approach is the use of n- and p-type materials connected with an ohmic junction ("photochemical diodes") to couple two photons into the overall chemical reaction.³¹

In particulate systems involving such dual light absorbers, special pains will have to be taken to avoid "short-circuiting" reactions of the intermediate redox species from greatly reducing the efficiency. One approach may be the immobilization of some of the redox couples on the surfaces within polymer layers.

An important apparent problem in the energetic analysis described above is the existence of "Fermi level pinning."³² Briefly, it appears that surface states within the semiconductor band gap, if present at a sufficiently high density, can pin the Fermi level in the semiconductor at a value that is less than the total gap energy. For example with both p-Si and p-GaAs maximum photovoltages of only ~ 0.6 V are obtained in liquid junction photocells. This would imply that larger band-gap materials may be required to drive the desired reactions. A positive aspect of Fermi level pinning is that the semiconductor band edges can be moved with respect to solution redox energy levels to carry out reactions which would not appear possible by consideration only of the semiconductor electrode energetics in the solution in the absence of redox couples. Surface treatment to decrease the extent of Fermi level pinning may be possible.

2. Kinetics. Recombination of the initially formed $e^- h^+$ pair, as well as intermediates on particulate systems, decreases the efficiency. The extent of recombination can be decreased by improving the kinetics of removal of e^- and h^+ to form final products. There is some evidence that

surface states and grain boundaries can act as recombination centers and methods of passivating these by specific chemical treatment have been proposed.³³

3. Stability. A key problem appears to be stability of the small band gap semiconductors to the reactive intermediates, e.g., those in the oxygen-evolution reaction, or to the very positive redox couples (D^+/D) needed to drive the oxidation. Various approaches, such as covering the surface with a passivating or polymer layer or employing surface modification are under investigation. The rapid removal of photogenerated charge and reactive intermediates by use of a catalyst on the electrode surface also promotes semiconductor stability. Another approach involves the use of larger band gap and stable semiconductors, e.g., TiO_2 , and a sensitizer layer (e.g., an organic dye, $Ru(bpy)_3^{2+}$,³⁴⁻³⁶ metal phthalocyanine³⁷) to allow the utilization of lower energy radiation. A number of examples of sensitized processes at semiconductors have been described, but so far the observed efficiencies have been rather low because thin sensitizer layers do not absorb sufficient quantities of light and thicker layers tend to be resistive. In some cases, recombination processes within the sensitizer layers and dye stability also appear to be problems. However, this approach, particularly with particle systems, is still under active investigation.^{23,38}

Conclusions

About a decade has passed since Honda and Fujishima³⁹ suggested that PEC cells based on single crystal n-type TiO_2 might be used for the photodecomposition of water to H_2 and O_2 . During this period much has been established about the behavior of the semiconductor/liquid interface and many new materials have been investigated. Particulate systems have been

devised and a number of different photocatalytic and photoelectrosynthetic methods have been developed. While the goal of an efficient and stable system for the direct solar production of fuels remains an elusive one, semiconductor-based systems remain the most efficient chemical systems described so far for such reactions. Moreover, research in photoelectrochemistry has led to an improved understanding of the semiconductor/liquid interface and the photoprocesses which occur there. It has also provided new insight into a variety of processes (electrochemical, photographic, catalytic, photolytic).

Acknowledgements

The support of the National Science Foundation (CHE 8000682), the Robert A. Welch Foundation, the Office of Naval Research, and the Solar Energy Research Institute is greatly appreciated.

REFERENCES

1. A.J. Bard, J. Photochem., 10, 50 (1979).
2. A.J. Bard, Science, 207, 139 (1980).
3. A.J. Nozik, Annu. Rev. Phys. Chem., 29, 189 (1978).
4. R. Memming, in Electroanalytical Chemistry, A.J. Bard, Ed., (Dekker, New York, 1979), pp. 1-84.
5. M. Wrighton, Acc. Chem. Res., 12, 303 (1979).
6. H. Gerischer, in Physical Chemistry--An Advanced Treatise, H. Eyring, D. Henderson, W. Jost, Eds., (Academic Press, New York, 1970), pp. 463-542.
7. S.R. Morrison, Electrochemistry at Semiconductor and Oxidized Metal Electrodes (Plenum, New York, 1980).
8. J.R. Bolton, Science, 202, 705 (1978).
9. A.J. Bard and M.S. Wrighton, J. Electrochem. Soc., 124, 1706 (1977).
10. H. Gerischer, J. Electroanal. Chem., 82, 133 (1977).
11. R. Noufi, A.J. Frank and A.J. Nozik, J. Am. Chem. Soc., 103, 1849 (1981).
12. A.B. Bocarsly, E.G. Walton, and M.S. Wrighton, ibid., 102, 3390 (1980).
13. (a) F-R. Fan, B.L. Wheeler, A.J. Bard and R. Noufi, J. Electrochem. Soc., 128, 2042 (1981); (b) T. Skotheim, I. Lundstrom and J. Prejza, ibid., 1625.
14. C.P. Kubiak, L.F. Schneemeyer and M.S. Wrighton, J. Am. Chem. Soc., 102, 6898 (1980).
15. F-R. Fan and A.J. Bard, J. Am. Chem. Soc., 102, 3677 (1980).
16. G. Nagasubramanian, A.S. Gioda, and A.J. Bard, J. Electrochem.

- Soc., 128, 2158 (1981).
17. H.S. White, H.D. Abruna and A.J. Bard, submitted for publication.
 18. D. Canfield and B. Parkinson, J. Am. Chem. Soc., 103, 1279 (1981).
 19. F-R. Fan, B. Reichman and A.J. Bard, J. Am. Chem. Soc., 102, 1488 (1980).
 20. D.C. Bookbinder, N.S. Lewis, M.G. Bradley, A.B. Bocarsly, and M.S. Wrighton, J. Am. Chem. Soc., 101, 7721 (1979).
 21. D. Miller, A.J. Bard, G. McLendon, and J. Ferguson, ibid., (in press).
 22. C.D. Jaeger and A.J. Bard, J. Phys. Chem., 83, 3146 (1979).
 23. E. Borgarello, J. Kiwi, E. Pelizzetti, M. Visca and M. Gratzel, Nature, 289, 158 (1981).
 24. B. Kraeutler and A.J. Bard, J. Am. Chem. Soc., 99, 7729 (1977); Nouv. J. Chim., 3, 31 (1979).
 25. (a) T. Inoue, A. Fujishima, S. Konishi, K. Honda, Nature (London), 277, 637 (1979); (b) M. Halmann, Nature, 275, 115 (1978).
 26. (a) I. Izumi, F-R. Fan, and A. J. Bard, J. Phys. Chem., 85, 218 (1981); (b) W.W. Dunn and A.J. Bard, Nouv. J. Chim. (in press).
 27. (a) S. Sato and J.M. White, Chem. Phys. Lett., 72, 83 (1980); (b) D. Duonghong, E. Borgarello, and M. Gratzel, J. Am. Chem. Soc., 103, 4685 (1981).
 28. See e.g., G. Munuera, A.R. Gonzales-Elipe, J. Soria, and J. Sanz, J.C.S. Faraday I, 76, 1535 (1980) and references therein.
 29. W.W. Dunn, Y. Aikawa, and A.J. Bard, J. Am. Chem. Soc., 103, 3456 (1981).
 30. M. Gratzel and R. Humphrey-Baker, private communication.

31. A.J. Nozik, Appl. Phys. Lett., 30, 567 (1977).
32. A.J. Bard, A.B. Bocarsly, F-R. Fan, E.G. Walton and M.S. Wrighton, J. Am. Chem. Soc., 102, 3671 (1980).
33. B.A. Parkinson, A. Heller and B. Miller, Appl. Phys. Lett., 33, 521 (1978).
34. W.D.K. Clark and N. Sutin, J. Am. Chem. Soc., 99, 4676 (1977).
35. H. Gerischer, Photochem. Photobiol., 16, 243 (1972), and references therein.
36. M. Gleria and R. Memming, Z. Phys. Chem. (Frankfurt am Main), 98, 303 (1975).
37. C.D. Jaeger, F-R. Fan and A.J. Bard, J. Am. Chem. Soc., 102, 2592 (1980); A. Giraudeau, F-R. Fan and A.J. Bard, ibid., 5137 (1980).
38. F-R. Fan and A.J. Bard, J. Am. Chem. Soc., 101, 6139 (1979).
39. A. Fujishima and K. Honda, Bull. Chem. Soc. Jpn., 44, 1148 (1971); Nature (London), 238, 37 (1972).

Figure Captions

Figure 1 - Schematic diagram of system for utilization of solar energy in a photoelectrosynthetic reaction (e.g., $H_2O \rightarrow H_2 + \frac{1}{2}O_2$). 1 and 2 represent the light-absorbing system and support; the dashed line around 1 and 2 represents a possible stabilizing layer on the system. 3 and 5 are redox couples, either in solution or incorporated onto the surface of the system; they act as the primary electron and hole acceptors. The final reaction is catalyzed by oxidation and reduction catalysts, CAT_O and CAT_R , respectively.

Figure 2 - Representative energetics for the system in Figure 1. The numbers at the energy levels represent potentials in V vs. NHE for the reactions at pH = 0. These potentials would shift by ~ 0.059 V per pH unit at 25°C, so that at pH 7, they would be about 0.4 V more negative.

Figure 3 - Schematic representation of (A) n-type semiconductor photoelectrochemical cells with typical values for the band edge locations for n-TiO₂ at pH = 0 (V vs. NHE). (B) p-type semiconductor cell with band edge locations for p-GaAs at pH = 0.

Figure 4 - Representation of effect of Pt in catalysis of hydrogen evolution reaction. Potentials at pH = 0 in V vs. NHE at right. ΔG_{ads} is the energy of adsorption of H-atoms on Pt. The relative location of H⁺ to H· and H₂ levels depends upon potential of the particle.

Figure 5 - The application of individual electrode (semiconductor and Pt) current-potential (i-V) curves in the design of

photoelectrochemical cells and particulate systems. Curves shown are for an n-type semiconductor (e.g., n-TiO₂) as shown in Figure 3A. The broken lines show the behavior for the oxidation ($D \rightarrow D^+$) and reduction ($O \rightarrow R$, e.g. H₂ evolution) at Pt and the solid lines at the irradiated semiconductor. The $D \rightarrow D^+$ reaction occurs at less positive potentials at the semiconductor because it is driven by light. a is the operating point for a semiconductor/Pt system and b is for the semiconductor alone. The higher currents at the operating point show that the platinized semiconductor should show a high reaction rate.

Figure 6 - Schematic diagram of a solar energy utilization system employing two light-absorbers and requiring two photons (at energies $h\nu_1$ and $h\nu_2$) to drive one electron through the system. The system is similar to that in Figure 1, except that an intermediate redox couple, O/R, connects the two light absorbing systems.

Figure 7 - Representative energetics for the system in Figure 6. See Figure 2 caption for other information.

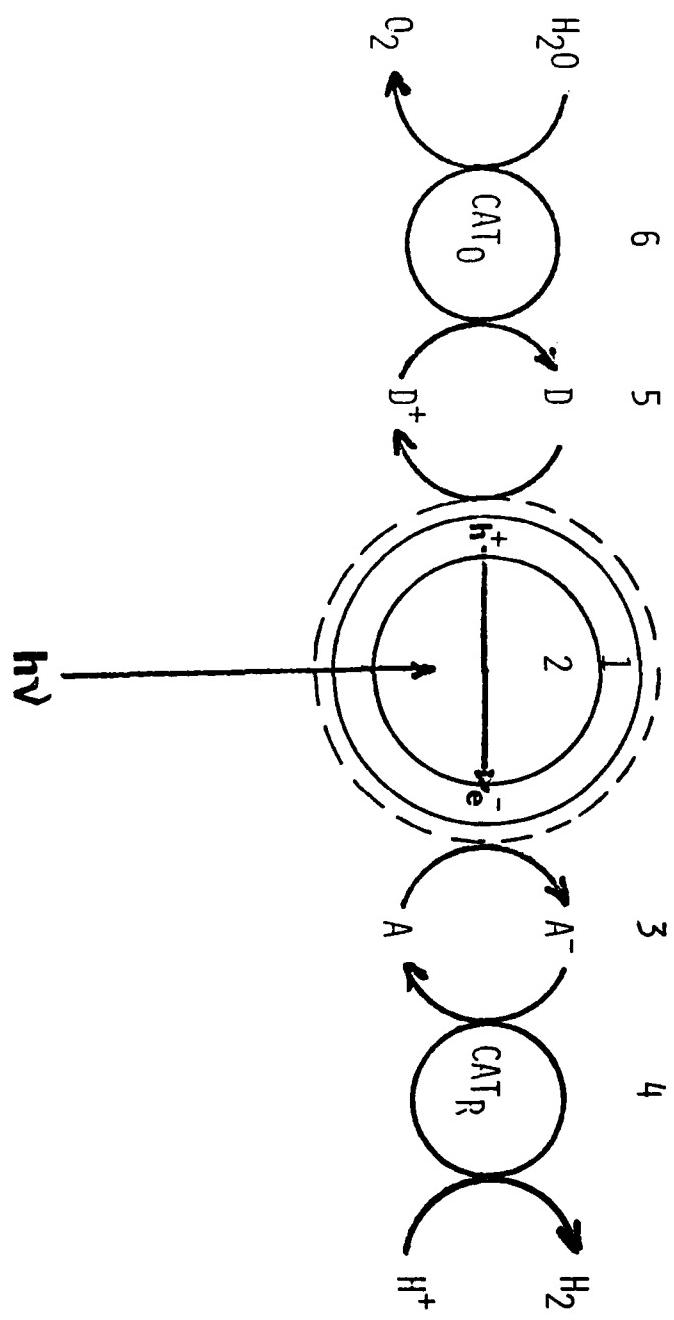


FIGURE 1

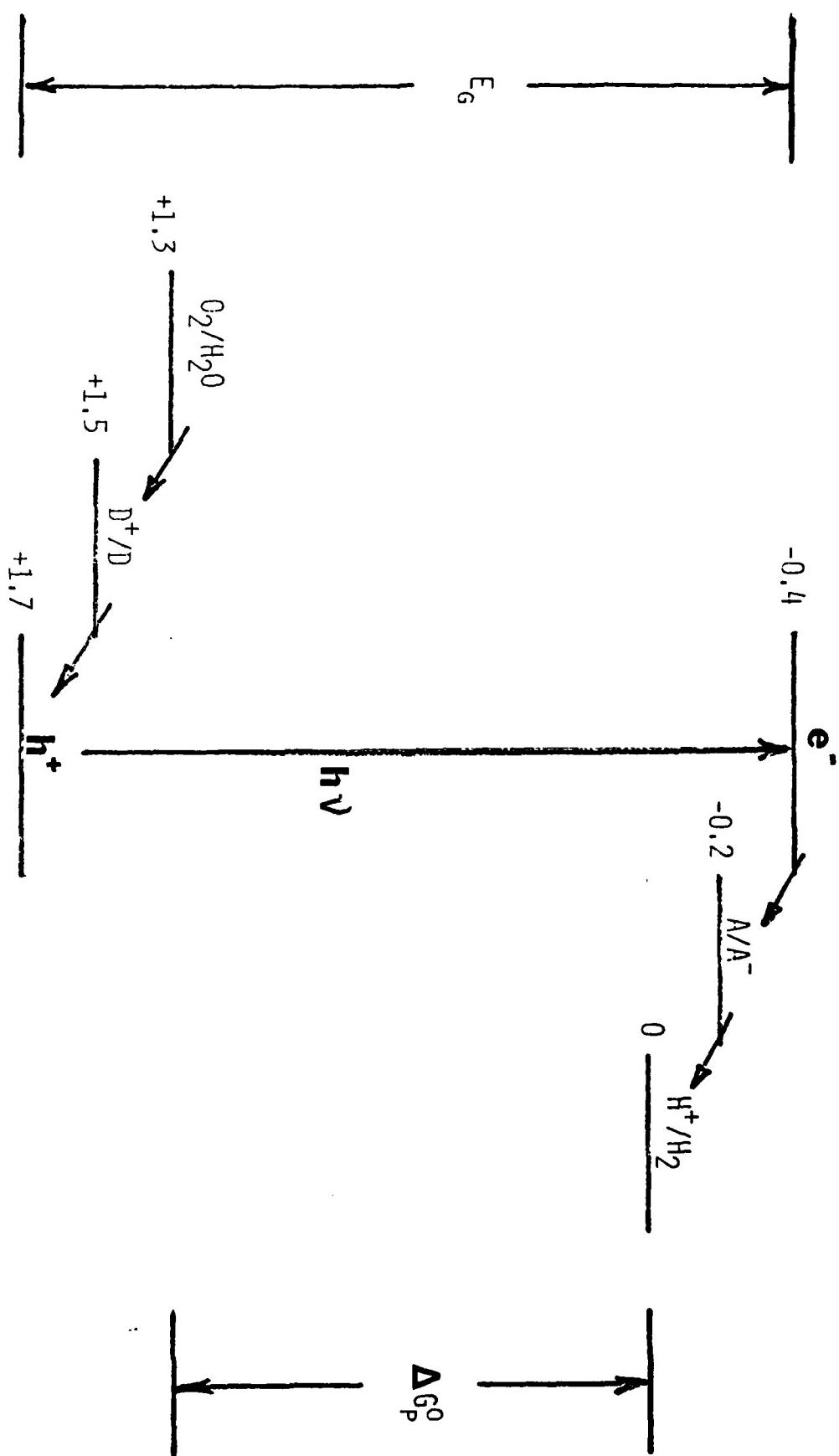
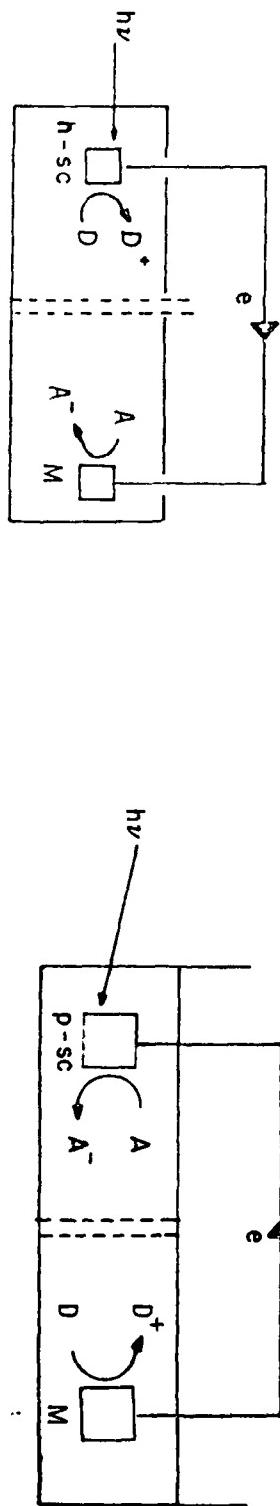


FIGURE 2

A



B

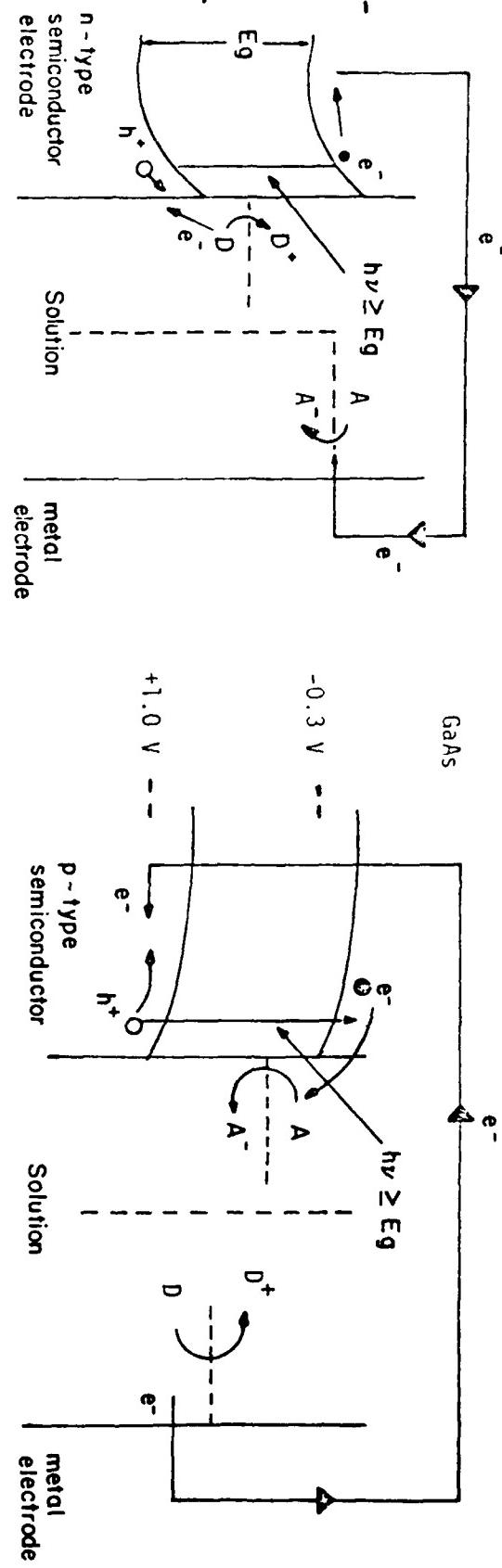


FIGURE 3

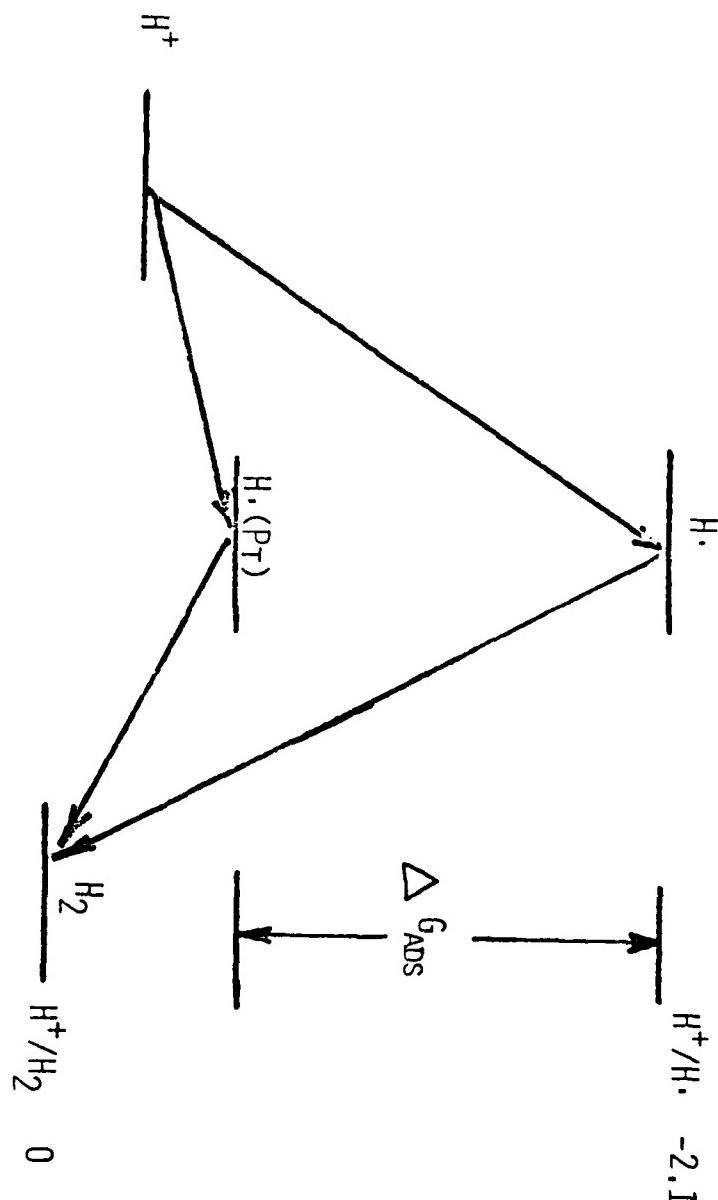


FIGURE 4

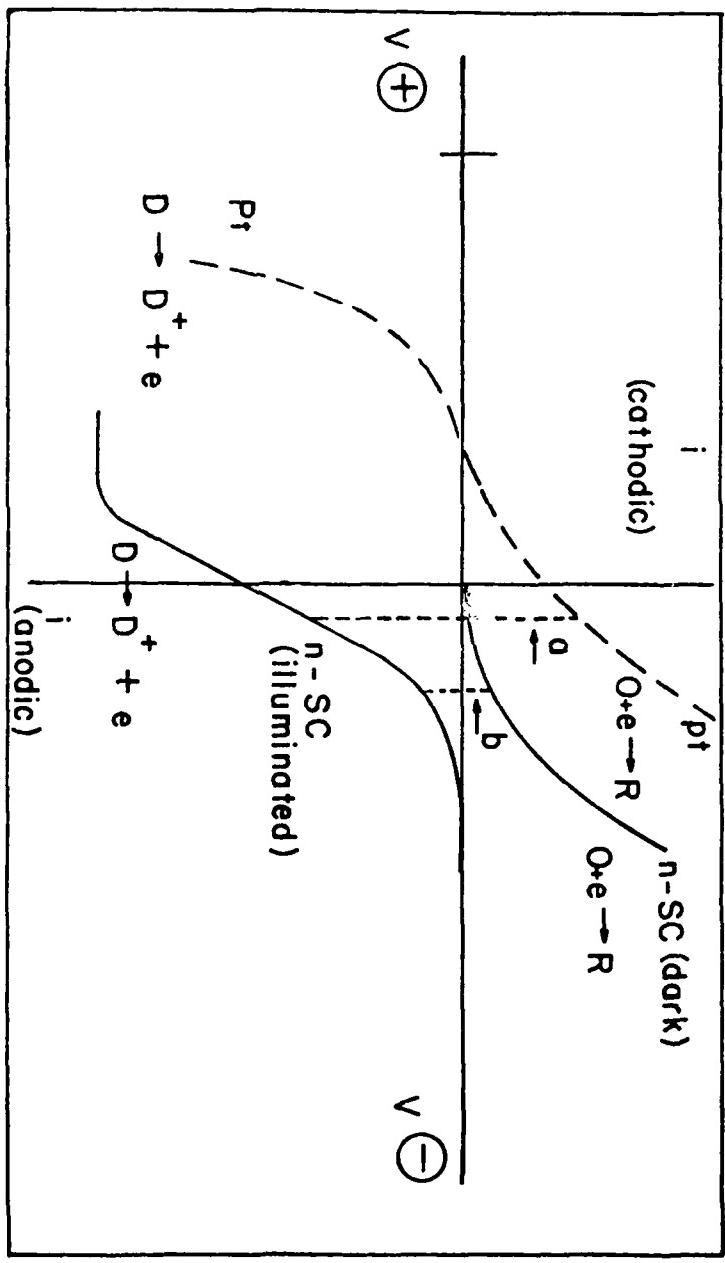


FIGURE 5

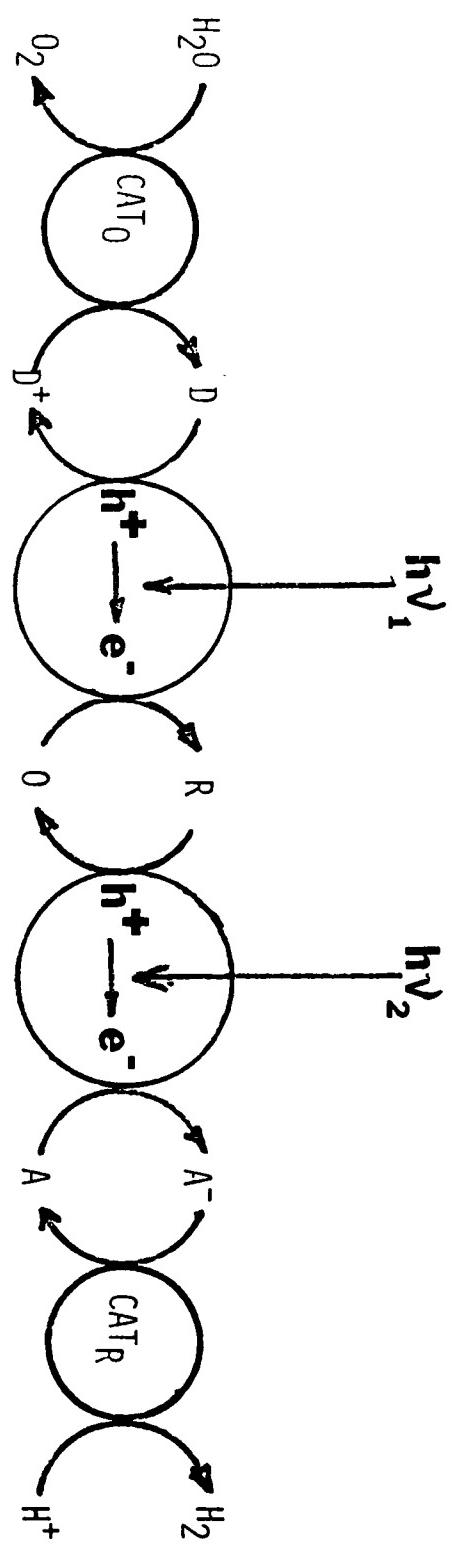


FIGURE 6

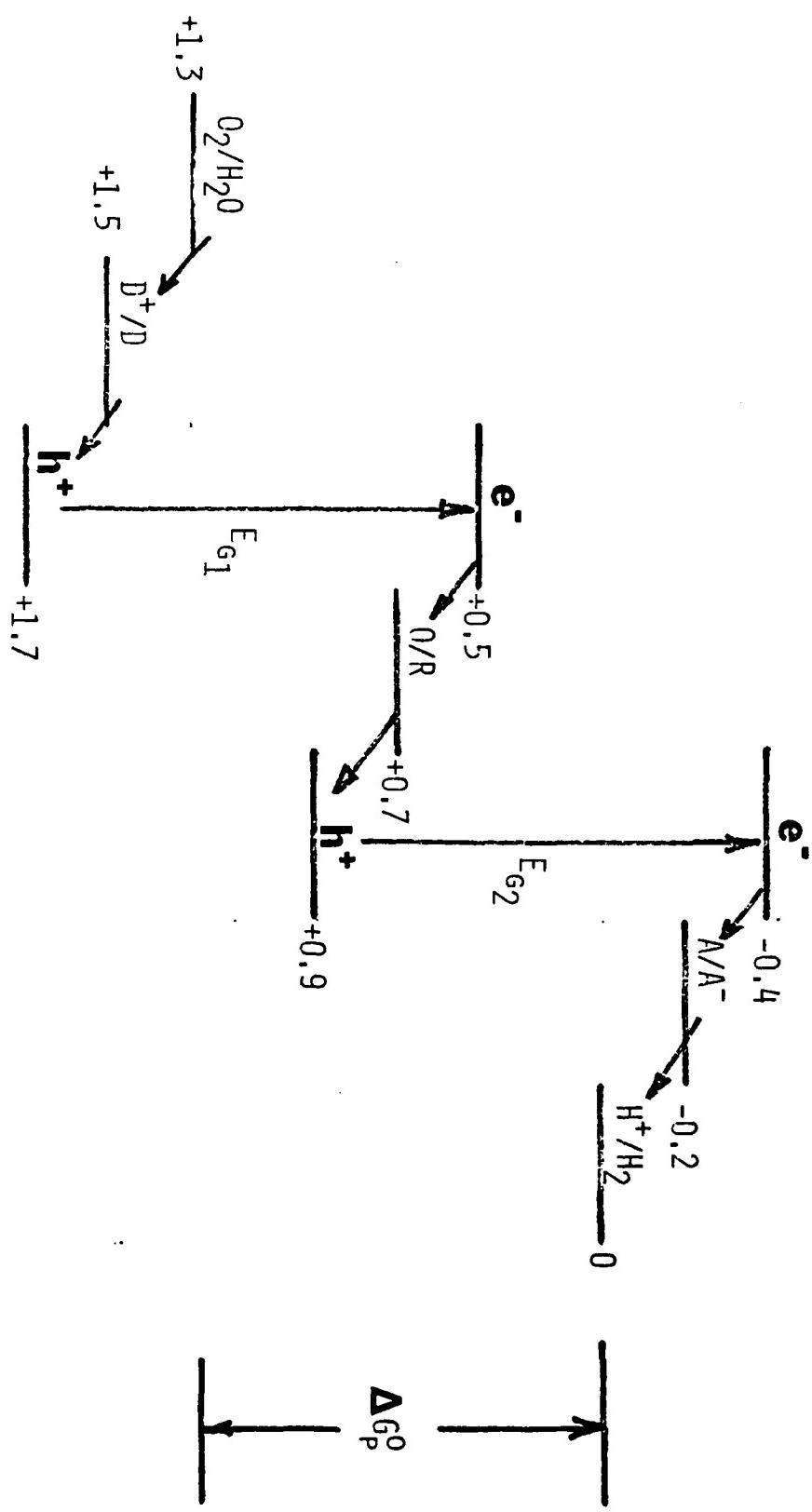


FIGURE 7

TECHNICAL REPORT DISTRIBUTION LIST, GEN

<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>	
Office of Naval Research Attn: Code 472 800 North Quincy Street Arlington, Virginia 22217	2	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 1211 Research Triangle Park, N.C. 27709	1
ONR Branch Office Attn: Dr. George Sandoz 536 S. Clark Street Chicago, Illinois 60605	1	Naval Ocean Systems Center Attn: Mr. Joe McCartney San Diego, California 92152	1
ONR Area Office Attn: Scientific Dept. 715 Broadway New York, New York 10003	+	Naval Weapons Center Attn: Dr. A. B. Amster, Chemistry Division China Lake, California 93555	1
ONR Western Regional Office 1030 East Green Street Pasadena, California 91106	1	Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1
ONR Eastern/Central Regional Office Attn: Dr. L. M. Peebles Building 114, Section D 666 Summer Street Boston, Massachusetts 02210	1	Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Director, Naval Research Laboratory Attn: Code 6100 Washington, D.C. 20390	1	Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
The Assistant Secretary of the Navy (RE&S) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1	Office of Naval Research Attn: Dr. Richard S. Miller 800 N. Quincy Street Arlington, Virginia 22217	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Department of the Navy Washington, D.C. 20360	1	Naval Ship Research and Development Center Attn: Dr. G. Bosmajian, Applied Chemistry Division Annapolis, Maryland 21401	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12	Naval Ocean Systems Center Attn: Dr. S. Yamamoto, Marine Sciences Division San Diego, California 91232	1
Dr. Fred Saalfeld Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1	Mr. John Doyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No.</u>	
	<u>Copies</u>	
Dr. Rudolph J. Marcus Office of Naval Research Scientific Liaison Group American Embassy APO San Francisco 96503	1	
Mr. James Kelley DTNSRDC Code 2803 Annapolis, Maryland 21402	1	

TECHNICAL REPORT DISTRIBUTION LIST, 359

<u>No.</u> <u>Copies</u>	<u>No.</u> <u>Copies</u>		
Dr. Paul Delahay Department of Chemistry New York University New York, New York 10003	1	Dr. P. J. Hendra Department of Chemistry University of Southampton Southampton SO9 5NH United Kingdom	1
Dr. E. Yeager Department of Chemistry Case Western Reserve University Cleveland, Ohio 44106	1	Dr. Sam Perone Department of Chemistry Purdue University West Lafayette, Indiana 47907	1
Dr. D. N. Bennion Department of Chemical Engineering Brigham Young University Provo, Utah 84602	1	Dr. Royce W. Murray Department of Chemistry University of North Carolina Chapel Hill, North Carolina 27514	1
Dr. R. A. Marcus Department of Chemistry California Institute of Technology Pasadena, California 91125	1	Naval Ocean Systems Center Attn: Technical Library San Diego, California 92152	1
Dr. J. J. Auborn Bell Laboratories Murray Hill, New Jersey 07974	1	Dr. C. F. Mueller The Electrochemistry Branch Materials Division, Research & Technology Department Naval Surface Weapons Center White Oak Laboratory Silver Spring, Maryland 20910	1
Dr. Adam Heller Bell Laboratories Murray Hill, New Jersey 07974	1	Dr. G. Goodman Globe-Union Incorporated 5757 North Green Bay Avenue Milwaukee, Wisconsin 53201	1
Dr. T. Katan Lockheed Missiles & Space Co., Inc. P.O. Box 504 Sunnyvale, California 94088	1	Dr. J. Boechler Electrochimica Corporation Attention: Technical Library 2485 Charleston Road Mountain View, California 94040	1
Dr. Joseph Singer, Code 302-1 NASA-Lewis 21000 Brookpark Road Cleveland, Ohio 44135	1	Dr. P. P. Schmidt Department of Chemistry Oakland University Rochester, Michigan 48063	1
Dr. B. Brummer EIC Incorporated 55 Chapel Street Newton, Massachusetts 02158	1	Dr. H. Richtol Chemistry Department Rensselaer Polytechnic Institute Troy, New York 12181	1
Library P. R. Mallory and Company, Inc. Northwest Industrial Park Burlington, Massachusetts 01803	1		

TECHNICAL REPORT DISTRIBUTION LIST, 359

<u>No.</u> <u>Copies</u>	<u>No.</u> <u>Copies</u>		
Dr. A. B. Ellis Chemistry Department University of Wisconsin Madison, Wisconsin 53706	1	Dr. R. P. Van Duyne Department of Chemistry Northwestern University Evanston, Illinois 60201	1
Dr. M. Wrighton Chemistry Department Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1	Dr. B. Stanley Pons Department of Chemistry University of Alberta Edmonton, Alberta CANADA T6G 2G2	1
Larry E. Plew Naval Weapons Support Center Code 30736, Building 2906 Crane, Indiana 47522	1	Dr. Michael J. Weaver Department of Chemistry Michigan State University East Lansing, Michigan 48824	1
S. Ruby DOF (STOR) 600 E Street Washington, D.C. 20545	1	Dr. R. David Rauh EIC Corporation 55 Chapel Street Newton, Massachusetts 02158	1
Dr. Aaron Wold Brown University Department of Chemistry Providence, Rhode Island 02192	1	Dr. J. David Margerum Research Laboratories Division Hughes Aircraft Company 3011 Malibu Canyon Road Malibu, California 90265	1
Dr. R. C. Chudacek McGraw-Edison Company Edison Battery Division Post Office Box 28 Bloomfield, New Jersey 07003	1	Dr. Martin Fleischmann Department of Chemistry University of Southampton Southampton SO9 5NH England	1
Dr. A. J. Bard University of Texas Department of Chemistry Austin, Texas 78712	1	Dr. Janet Ostervoung Department of Chemistry State University of New York at Buffalo Buffalo, New York 14214	1
Dr. M. M. Nicholson Electronics Research Center Rockwell International 3370 Miraloma Avenue Anaheim, California	1	Dr. R. A. Osteryoung Department of Chemistry State University of New York at Buffalo Buffalo, New York 14214	1
Dr. Donald W. Ernst Naval Surface Weapons Center Code R-33 White Oak Laboratory Silver Spring, Maryland 20910	1	Mr. James R. Moden Naval Underwater Systems Center Code 3632 Newport, Rhode Island 02840	1

TECHNICAL REPORT DISTRIBUTION LIST, 359

<u>No.</u> <u>Copies</u>	<u>No.</u> <u>Copies</u>		
Dr. R. Nowak Naval Research Laboratory Code 6130 Washington, D.C. 20375	1	Dr. John Kincaid Department of the Navy Strategic Systems Project Office Room 901 Washington, DC 20376	1
Dr. John F. Houlihan Shenango Valley Campus Pennsylvania State University Sharon, Pennsylvania 16146	1	M. L. Robertson Manager, Electrochemical Power Sonices Division Naval Weapons Support Center Crane, Indiana 47522	1
Dr. M. G. Sceats Department of Chemistry University of Rochester Rochester, New York 14627	1	Dr. Elton Cairns Energy & Environment Division Lawrence Berkeley Laboratory University of California Berkeley, California 94720	1
Dr. D. F. Shriver Department of Chemistry Northwestern University Evanston, Illinois 60201	1	Dr. Bernard Spielvogel U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709	1
Dr. D. H. Whitmore Department of Materials Science Northwestern University Evanston, Illinois 60201	1	Dr. Denton Elliott Air Force Office of Scientific Research Bldg. 104 Bolling AFB Washington, DC 20332	1
Dr. Alan Bewick Department of Chemistry The University Southampton, SO9 5NH England	1	Dr. A. Himy NAVSEA-5433 NC #4 2541 Jefferson Davis Highway Arlington, Virginia 20362	1

